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EVIDENCE FOR HOMOGENEOUS DISTRIBUTION OF GAMMA-ACTIVE ISOTOPES IN UTS-5

C.W. Smith
Chemical Laboratory

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EVIDENCE FOR HOMOGENEOUS DISTRIBUTION OF GAMMA-ACTIVE ISOTOPES IN UTS-5

by

C.W. Smith*

ABSTRACT

UTS-5 was prepared by dilution blending of a reference uranium/thorium ore with silica as a blind control reference for an interlaboratory program to establish radioisotope activities in tailings reference materials. These are intended for use as quality control samples in the Measurement Program, National Uranium Tailings Research Program. Gamma-ray spectrometry measurements of one-gram subsamples of UTS-5 and the source ore are analysed statistically to estimate the degree of homogeneity of the blend with respect to total gamma-active isotopes. The coefficient of variation is found to be less than 0.7%. Independent estimates of counting statistics and measurement-precision demonstrate that these are minor components of the observed variance. The variance component due to sample pelletizing (geometry/mass variance) could not be independently estimated. Consequently only an upper limit could be established for the variance due to inhomogeneity. The gamma activity ratio UTS-5/source ore measured 0.494 ± .005 for one-gram subsamples, consistent with the mass dilution ratio and independent uranium concentration measurements.

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*Research Scientist, Chemical Laboratory, Mineral Sciences Laboratories.

INTRODUCTION

The material UTS-5 is incorporated as a reference check sample in a multi-laboratory certification program to establish activity levels of various isotopes in a series of uranium mill tailings reference samples, designated UTS-1 to UTS-4 (1). These materials are intended for use in a quality-assurance program to be conducted in conjunction with the Measurement Program aspect of the National Uranium Tailings Research Program (NUTRP) (2).

UTS-5 is in fact a 1:1 blend of the CCRMP uranium/thorium reference ore DH-1a with floated silica powder (3). Since DH-1a is currently undergoing a certification program for several important constituent isotope activities and contains activities from both uranium and thorium decay series, it was judged to be a viable check sample to support the integrity of the UTS-series certification program (4).

The purpose of silica dilution was threefold; to disguise the source identity, to bring isotope activities into a realistic activity range for tailings materials, and to test the viability of silica dilution for possible future application in the quality assurance program. Dilution was accomplished by thoroughly blending weighed quantities of DH-1a and Fisher floated-silica powder using a small cone blender. (Masses were 1.000 kg each; and blending was carried out for 16 hours; this was followed by bottling in 100 g lots). The silica material is known from previous measurements to contain negligible radioactive contaminants (5).

The measurements described herein were carried out to establish that the blend was sufficiently homogeneous so that a distribution of isotope activities in subsamples would not predominate in determining the between-sample measurement precision. Various physical factors are known to affect both original homogeneity and subsequent segregation in solid particle blending (6). The similar powder densities and particle size distributions of the components in this instance tend to favour homogeneous blending (7).

METHOD

Gamma-Ray Emission Measurements

Gamma-ray spectrometry provides a convenient means of measuring relative isotope activities. Relative intensities of specific photopeaks can provide measurements of individual gamma-active isotopes. Practical consider-

ations however lobbied against measurement of individual gamma-ray photopeaks in this instance, since it was necessary to demonstrate homogeneity of one-gram subsample amounts. At this quantity, counting times required to adequately minimize the statistical uncertainty in individual net photopeak areas were prohibitively long. Instead, the total gamma-ray emission intensity over specific energy ranges was monitored to yield an estimate of the combined homogeneity of gamma-emitting isotopes.

An "equilibrium" uranium ore (Sill's ore*), N.B.S. uranium oxide, and aged thorium nitrate were used to estimate the relative contributions of the principle component series isotopes (8-10). As shown in Table 1, the intensities observed for a 2.5 g sample of DH-1a could be accurately predicted from derived component intensities and the certified (parent) concentration values. The radium series contribution was derived from the difference between the equilibrium uranium ore and uranium oxide spectral contributions.

The relative contributions of the three "series" components to the total gamma-ray intensity, calculated from the data of Table 1 and an ambient background measurement appear in Table 2. The principle contributions from the radium series are ^{214}Bi, ^{214}Pb, ^{226}Ra, and X-rays; those from the uranium group are principally ^{234}Pa, ^{234}Th, ^{235}U, and X-rays. The thorium series contributors are predominantly ^{228}Ac, ^{208}Tl, ^{212}Pb, ^{212}Bi and X-rays. Table 2 shows that the relative make-up of the total gamma-ray intensity is remarkably constant, with radium-series isotopes predominating. This is in large part due to the minor role of photopeaks in determining the total spectral intensity. Compton scattered gamma-rays, arising from all higher energy components, contribute 75% of the intensity. The Compton fraction was estimated by summing all principle photopeak areas in the DH-1a spectrum.

Comparison of observed total gamma-ray intensities between samples thus measures the mean distribution of all emitting isotopes. Since individual energy regions in the calibration range offer no appreciable difference in sensitivity to different isotopes, only the full range intensity (where

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*A sample of this material, obtained from the Idaho Falls Operations Office, U.S. Department of Energy, was stated to contain 0.973 ± .004 % U_3O_8. Measurements of several ^{238}U series isotopes suggest this series is in secular equilibrium (8).

superior counting statistics are obtained) was subjected to statistical analysis.

Randomly selected one-gram sub-samples were transferred to 3.18 cm diameter aluminum caps and pressed into a disc at 138 MPa for 1 minute. The discs were mounted axially face-down on a mylar film on the end window of a true coaxial high-purity germanium gamma-ray detector having an active volume of 56 cm^3 and a conventional efficiency of 13%. Gamma-ray spectra from 15 to 1440 keV were acquired typically for 4500 s.

Statistical Treatment

It is assumed that significant inhomogeneity would be observed as a normal distribution of gamma-ray activity characterized by a standard deviation, SIN, about a mean, $\bar{R}$. It is also assumed that the observable standard deviation, SO, is the resultant of several normally distributed components which are independent, i.e., having zero covariance, so that

$$SO^2 = \Sigma S_i^2 = SIN^2 + SD^2 + SRC^2 + SS^2$$

The components (S_i) are: SIN (defined above); SRC, the standard deviation attributed to counting statistics (which may be predicted); SS, the standard deviation of measurement reproducibility for a single sample (beyond that attributable to counting statistics); and SD, the disc pressing reproducibility, incorporating any variation in the disc geometry or material loss, and weighing precision. Since SD cannot be measured independently without a known, totally homogeneous similar material, we define $SI = (SIN^2 + SD^2)^{1/2}$, as the combined inhomogeneity/disc-reproducibility parameter, to be determined.

The following method is employed to calculate % SI, the relative standard deviation attributable to inhomogeneity and disc reproducibility:

(1) $SO = [\sum_i^n (R_i - \bar{R})^2/(n-1)]^{1/2}$, where R_i is the observed and $\bar{R}$ the mean count rate, resp.; and n, the number of observations.

(2) $S\bar{R} = SO/n^{1/2}$, the standard deviation of the mean, $\bar{R}$.

(3) $S\bar{R}C = [\sum_{i}^{n} (SR_i)^2]^{1/2}/n$, the standard deviation of $\bar{R}$ predicted from counting statistics, where

(3a) $SR_i = N^{1/2}/T$, the standard deviation R_i due to counting statistics; N is the observed count integral, and T the time (11).

(4) $DS\bar{R} = (S\bar{R}^2 - S\bar{R}C)^{1/2}$, the residual standard deviation in $\bar{R}$.

(5) $SIR = DS\bar{R} \times n^{1/2}$, the non-counting statistics standard deviation component for individual measurment.

(6) $\%SI = [(100\ SIR/\bar{R})^2 - \%\ SS^2]^{1/2}$, the relative standard deviation attributed to inhomogeneity plus disc irreproducibility, where

(6a) $\%SS = 100\ SS/\bar{R}(STD)$, the individual measurement reproducibility for a single pellet, where

(6b) $SS = (SO^2 - (\sum_{i}^{n} SR_i^2)/n)^{1/2}$, the non-counting statistics component of the standard deviation observed for repeated measurements of the same pellet.

The following statistical tests were applied:

(1) Is $S\bar{R}$ significantly greater than $S\bar{R}C$ at the 95% confidence level?

Test: $S\bar{R}.A_{.05,f} > S\bar{R}C$, where f is the degrees of freedom in the determination of $S\bar{R}$, and $A_{.05,f}$ is obtained from Table A-21, reference (12).

(2) Welch's test for equality of within-bottle (W) and between-bottle (B) subsample means:

Is $\bar{R}_W = \bar{R}_B$, at the 95% confidence level?

$$t' = (\bar{R}_B - \bar{R}_W)/(S\bar{R}_B^2 + S\bar{R}_W^2)^{1/2}$$

$$c = S\bar{R}_B^2/(S\bar{R}_B^2 + S\bar{R}_W^2)$$

$$f = 1/[c^2/f_W^2 + (1-c)^2/f_B^2], \quad f = \text{degrees of freedom}$$

Test: If $t' < t_{.05,f}$ the null hypothesis is accepted (13).

(3) Are the values for % SI within- and between-bottles significantly different?

Are the values for % SI for UTS-5 and DH-1a significantly different?

$$F' = \%SI_W/\%SI_B$$
$$F'' = \%SI_{DH}/\%SI_B$$

Test:

If $F' < F_{.05\ 2\text{-sided},f_W/f_B}$ the values are not significantly different.

If $F'' < F_{.05,\ 2\text{-sided},\ f_{DH}/f_B}$ the values are not significantly different (13).

RESULTS

The gamma-emission data are summarized in Tables 3 and 4, and the statistical results appear in Tables 5-8.

The data of Table 3 indicate that the system response and measurement geometry could be reproduced with a relative standard deviation of 0.14% throughout the course of the measurements.

Comparison of the last two columns of Table 6 indicates that the observed variance is in large fraction attributable to the combined variance of pelletizing and inhomogeneity, and not to measurement irreproducibility nor counting statistics. In all cases observed variances were found to be significantly larger than those predicted on the basis of counting statistics.

Welch's test for equality of the withinand between-bottle means was deemed to be appropriate in view of the relatively small sample size and apparent difference between the mean standard deviations (13). Table 8 indicates that the variances attributed to the combined inhomogeneity/pelletizing precisions are comparable for DH-1a and UTS-5. Homogeneity of uranium in DH-1a has been demonstrated. The observed relative standard deviation was

0.36% for determinations of uranium in 45 sub-samples (3). Gamma-ray measurements of radium-226 in DH-1a had a standard deviation of 0.46% when four 75 g sub-samples were measured (5). It is probable, therefore, that the distribution of ^{226}Ra in DH-1a sub-samples is characterized by a standard deviation which is less than about 0.4%.

In the present measurements of DH-1a, % SI (which measures inhomogeneity combined with pelletizing precision) was 0.76%. The above information suggests that the pelletizing component predominates in determining this value. Since % SI obtained for UTS-5 is not significantly different than this value, it may be concluded that the ^{226}Ra homogeneity was not detectably degraded by the silica dilution.

The mean gamma-ray intensity ratio UTS-5/DH-1a for one gram sub-samples is consistent with the mass dilution and measured uranium concentrations (Table 9).

CONCLUSION

The degree to which homogeneity of gamma-active isotopes can be established is limited by the precision of the measurement methodology. An upper limit coefficient of variation of about 0.7% for gamma-ray activity of one-gram sub-samples of UTS-5 has been established. It is highly probable that the actual coefficient of variation of gamma-active isotopes is smaller than this figure. It is consequently possible to quantitatively relate activities found in sub-samples of UTS-5 to those present in DH-1a.

It is apparent that homogeneous dilutions of powdered reference materials with silica can successfully be obtained.

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Table 1 - Calculated spectral intensity contribution from 2.5 g of DH-1a

	Intensity, $s^{-1}g^{-1}$ (U or Th)				
Region:	1	2	3	4	5
keV:	16-1440	190-1440	250-1440	16-180	180-620
U Ore	6366 (18)	2989 (11)	2525 (10)	3187 (11)	2369 (9)
U_3O_8/SiO_2	1099 (2)	350 (1)	296 (1)	693 (2)	294 (1)
"Radium", calc	5267 (18)	2639 (11)	2229 (10)	2494 (11)	2075 (9)
Th/SiO_2	2202 (7)	1086 (5)	745 (4)	1094 (5)	848 (4)
DH-1a, calc	46.85 (.15)	22.12 (.08)	18.29 (.07)	23.44 (.09)	17.50 (.07)
DH-1a, obsvd	46.75 (.12)	22.13 (.08)	18.20 (.08)	23.36 (.09)	17.53 (.07)

Numbers in brackets are 1σ uncertainties propagated from concentration and counting statistics components.

Table 2 - Calculated relative intensity contributions of series isotopes, UTS-5

	Percentage of Total Intensity				
Region:	1	2	3	4	5
Radium	66.5	69.1	70.6	58.5	68.0
Uranium	14.0	10.5	10.8	23.1	11.1
Thorium	9.7	9.6	8.3	9.9	9.8
Background	9.8	10.8	10.3	8.5	11.1
Compton	74	75	75	74	67

Table 3 - Measurement reproducibility. A single reference pellet of BL-5 was counted repeatedly interspersed with the experimental measurements

Measurement	Count Rate, s^{-1}	SR_i
1	1125.6	0.7
2	1129.0	1.1
3	1131.6	0.7
4	1132.7	0.7
5	1131.4	0.6
6	1130.7	1.1
7	1130.3	0.7
8	1128.7	0.7
9	1127.9	0.7
10	1129.3	0.7
$\bar{R}$	1129.7	$(\Sigma SR_i^2)/n = 0.62$
SO	1.8	
SS	1.6	
%SS	0.14	

Table 4 - Count rates observed for one gram sub-samples of UTS-5 and DH-1a 15.9 to 1440.2 keV

Bottle		Count Rate, $s^{-1}g^{-1}$
700	A	11.43
	B	11.28
	C	11.52
	D	11.29
	E	11.32
	F	11.32
701		11.45
702		11.43, 11.23
703		11.40
704		11.38
705		11.48, 11.28, 11.45
706		11.46, 11.32
707		11.21, 11.26
708		11.46
709		11.28
DH-1a	A	22.26
	B	21.82
	C	21.80
	D	21.74
	E	21.99
	F	21.86
	G	21.81

S_{Ri} (UTS-5) = 0.05 in all cases.

S_{Ri} (DH-1a) = 0.04, 0.04, 0.07, 0.06, 0.07, 0.07, 0.04, resp.

Table 5 - Statistical results

	f	$\bar{R}$	SO	$S\bar{R}$	$S\bar{R}C$
Bottle 700	5	11.36	.095	.039	.020
All bottles	9*	11.37	.070	.022	.002
DH-1a	6	21.90	.18	.067	.022

*mean results for bottle 700 used as single value

Table 6 - Analysis of components of variance

	$DS\bar{R}$	SIR	% SIR	% SI	% SO
Bottle 700	.033	.081	.71	.70	.84
All bottles	.022	.069	.61	.59	.62
DH-1a	.064	.17	.77	.76	.82

Table 7 - Analysis of variance. Null hypothesis is equality of within- and between-bottle means for UTS-5 (Welch's test)

	$\bar{R}$	$(S\bar{R})^2$	f	t'	$t_{.05,f}$
Within-bottle	11.36	0.0015	5		
Between-bottle	11.37	0.00048	9		
Test			8	0.22	2.3
Null hypothesis			accepted		

Table 8 - Analysis of variance. Null hypothesis are equality of relative standard deviations (a) within- and between-bottles for UTS-5, and (b) for UTS-5 and DH-1a

	$(\% SI)^2$	f	F'	$F_{.05,f_1/f_2}$	Null Hypothesis
Within-bottle	.49	5			
Between-bottle	.35	9			
DH-1a	.58	6			
Test (a)			1.4	4.48	accepted
Test (b)			1.6	4.32	accepted

Table 9 - Activity and uranium ratios, UTS-5/DH-1a

	Gamma-ray intensity		Uranium	
	Net* s^{-1}	95% CL (%)	%U	95% CL(%)
UTS-5	10.26	0.57	0.1299	~0.77
DH-1a	20.79	0.80	0.2629	0.15
Ratio	0.494	0.98	0.494	0.77

*Background is 1.112 ± .015 s^{-1}, 1σ